The CONCEPTUAL DEVELOPMENT *of* QUANTUM MECHANICS

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2 Early Applications of Quantum Conceptions to Line Spectra

2.1 Regularities in Line Spectra

In the preceding chapter we saw how the study of the single physical phenomenon of black-body radiation led to the conceptions of quanta and to the quantum statistics of the harmonic oscillator, and thus to results which defied the principles of classical mechanics and, in particular, the equipartition theorem. It was generally agreed that classical physics was incapable of accounting for atomic or molecular processes. But how to modify classical physics by new conceptions was as yet an open question.

It was clear that further progress was contingent upon a broadening of the scope of pertinent physical phenomena. Indeed, it was the study of the discrete spectra of the chemical elements which constituted the next stage of development after the study of the continuous spectra[1] of thermal radiation and contributed decidedly to the development of quantum theory.

Ever since Newton laid the foundations of spectroscopy in 1666, the question concerning the origin of spectral lines had been regarded as an important problem in physics. Late-nineteenth-century physicists interpreted the spectrum of a given element in a way analogous to the acoustic vibrations of a sound-producing body. They assumed that the whole spectrum of a given element originated in the natural periods of oscillations of one and the same atom. Thus, to mention only one example, Herschel inferred from Balmer's famous formula that atomic processes resemble acoustic phenomena in organ pipes.[2]

[1] As shown in the beginning of the preceding chapter, Kirchhoff's law and, in its wake, the study of black-body radiation had their historical origin in the investigation of the Fraunhofer lines, that is, ultimately in a question pertaining also to discrete spectra.

[2] A. S. Herschel, "On a relation between the spectrum of hydrogen and acoustics," *Astrophysical Journal 7*, 150–155 (1898).

Mitscherlich[3] was the first to point out that spectroscopy should be regarded not only as a method of chemical analysis—spectroanalysis had just recorded its first spectacular achievements—but also as a clue to the secrets of the inner structure of the atom and the molecule. His own research, however, was confined to a merely qualitative comparison of different spectra of elements and compounds. Five years later, Mascart[4] was the first to draw attention to the existence of definite arithmetical relations between the wavelengths of certain lines in the same spectrum. He interpreted the double lines in the spectrum of sodium and the triplets in that of magnesium as harmonic vibrations. Inspired by Mascart's remarks, Lecoq de Boisbaudran[5] in 1869 thought he had found that the spectral lines of nitrogen, whose wavelengths he measured in units of 10^{-6} mm, exhibit similar harmonic relations. He tried to show that this spectrum is made up of two sets of bands, one extending from the red to the green and the other from the green to the violet, and that each band of the second set had a wavelength which was in the ratio of three to four with that of a corresponding band of the first set. Although soon disproved by R. Thalèn, a pupil of Ångström, Lecoq's paper inaugurated an intensive search for numerical regularities in spectra.[6] The first study of the spectrum of hydrogen, from this point of view, was made by G. Johnstone Stoney. In accordance with his basic assumption "that the lines in the spectra of gases are to be referred to periodic motions within the individual molecule, and not to the irregular journeys of the molecules amongst one another,"[7] Stoney declared that "one periodic motion in the molecule of the incandescent gas may be the source of a whole series of lines in the spectrum of the gas,"[8] an idea which, if mathematically formulated, would have led him to a Fourier analysis of the motion. To substantiate his claim, Stoney

[3] A. Mitscherlich, "Ueber die Spectren der Verbindungen und der einfachen Körper," *Poggendorff's Annalen der Physik 121*, 459–488 (1864).

[4] M. Mascart, "Sur les spectres ultraviolets," *Comptes Rendus 69*, 337–338 (1869). On p. 338 he wrote: "Un problème important, qui doit se proposer l'analyse spectrale, est de savoir s'il existe une relation entre les différentes raies d'une même substance ou bien entre les spectres de substances analogues. J'ai observé, en 1863, que les six raies principales du sodium, aperçues pour la première fois par MM. Wolf et Diacon, sont doubles, et que les deux raies qui constituent chacun des groupes sont à peu près à la même distance que celle de la double raie. Cela parait être la répétition d'un même phénomène en différents points de l'échelle spectrale." With reference to the magnesium triplets he declared: "Il me semble difficile que la reproduction d'un pareil phénomène soit un effet du hasard; n'est-il pas plus naturel d'admettre que ces groupes de raies semblables sont des harmoniques qui tiennent à la constitution moléculaire du gaz lumineux?" *Ibid.*

[5] Lecoq de Boisbaudran, "Sur la constitution des spectres lumineux," *Comptes Rendus 69*, 445–451, 606–615, 657–664, 694–700 (1869).

[6] Cf., for example, J. L. Soret, "On harmonic ratios in spectra," *Philosophical Magazine 42*, 464–465 (1871).

[7] G. J. Stoney, "The internal motions of gases compared with the motions of waves of light," *Philosophical Magazine 36*, 132–141 (1868).

[8] G. J. Stoney, "On the cause of the interrupted spectra of gases," *Philosophical Magazine 41*, 291–296 (1871).

referred to Angström's[9] famous measurements of the wavelengths of the four then known hydrogen spectral lines: 6562.10×10^{-7} mm, 4860.74×10^{-7} mm, 4340.10×10^{-7} mm, and 4101.2×10^{-7} mm. Stoney contended that three of these lines, namely, those with wavelengths, if reduced to vacuum, $\lambda_1 = 6563.93 \times 10^{-7}$ mm, $\lambda_2 = 4862.11 \times 10^{-7}$ mm, and $\lambda_3 = 4102.37 \times 10^{-7}$ mm, "are to be referred to the same motion in the molecule of the gas"[10] and are "the 20th, 27th and 32nd harmonics of a fundamental vibration whose wavelength in vacuo" is $\lambda_0 = 0.13127714$ mm.[11]

Although forced to admit that "the other harmonics (19th, 21st, 22nd) are not found in this spectrum of hydrogen," Stoney was confident that further examinations would eventually establish additional harmonics.[12] In carrying out this research, subsequently with the assistance of Dr. Reynolds of Dublin,[13] Stoney found it "convenient to refer the positions of all lines in the spectrum to a scale of reciprocals of the wave-lengths"[14] rather than to that of wavelengths used so far. His reasons for this innovation were as follows: "This scale has the great convenience, for the purposes of the investigation, that a system of lines with periodic times that are harmonics of one periodic time are equidistant upon it; and it has the further convenience, which recommends it for general use, that it resembles the spectrum as seen in the spectroscope much more closely than the scale of direct wave-lengths used by Ångström in his classic map." And Stoney continued: "If, then, k be the wave-number of a fundamental motion in the aether, its wave-length will be $1/k$ of a millimeter, and its harmonics will have the wave-lengths $1/2k$, $1/3k$, etc., in other words, they occupy the positions $2k$, $3k$, etc., upon the new map."

Stoney—the same Stoney who twenty-three years later introduced the term "electron" into physics—thus was the first to define the subsequently so important notion "wave-number." Even his original notation (k) is common usage in modern theoretical physics, where it generally denotes—for the sake of further computational convenience—the number of waves in 2π units of length (2π cm) rather than per millimeter as proposed by Stoney.

[9] A. Ångström, *Recherches sur le Spectre Solaire* (Upsala, 1868), p. 31. Ångström's table of wavelengths, published in this book, served for a long time as a standard for spectroscopists.

[10] REF. 8 (1871), p. 294.

[11] These are, of course, the lines H_α, H_β, and H_δ of the Balmer series which satisfy the relations $\lambda_1 = \lambda_0/20$, $\lambda_2 = \lambda_0/27$, and $\lambda_3 = \lambda_0/32$.

[12] The other lines of the Balmer series, down to 3699 Å, were discovered a few years later in the ultraviolet spectra of Sirius and other white stars by the English astronomer W. Huggins and published in his paper "Sur les spectres photographiques des étoiles," *Comptes Rendus* *90*, 70–73 (1880).

[13] G. J. Stoney and J. E. Reynolds, "An inquiry into the cause of the interrupted spectra of gases," *Philosophical Magazine* *42*, 41–52 (1871).

[14] G. J. Stoney, "On the advantage of referring the position of lines in the spectrum to a scale of wave-numbers," *British Association Reports, Edinburgh*, *41*, pp. 42–43 (1871).

It was in the course of similar investigations that Liveing and Dewar[15] discovered in the spectra of sodium and potassium the existence of two series of lines, one of sharp and one of diffuse lines, and established[16] the existence of homologous series, that is, series of lines of the same type in chemically analogous elements. At the same time, Arthur Schuster stressed the importance of the search for "an empirical law connecting the different periods of vibration in which we know one and the same molecule to be capable of swinging."[17] He even applied the theory of probability to calculate the accidental occurrence of harmonic ratios on the assumption that no such law exists and that all lines are distributed at random. Having thus tested the statistical significance of the available data, Schuster[18] concluded that "most probably some law hitherto undiscovered exists which in special cases resolves itself into the law of harmonic ratios."

Three years later, such an empirical formula, the first to comprise correctly all lines of a spectral series, was published by Johann Jakob Balmer, a schoolteacher in Basel.[19] His first paper, published in the *Verhandlungen der Naturforschenden Gesellschaft in Basel* (*Proceedings of the Scientific Society of Basel*) for the year 1885, contained the prophetic words: "It appears to me that hydrogen . . . more than any other substance is destined to open new paths to the knowledge of the structure of matter and its properties. In this respect the numerical relations among the wavelengths of the first four hydrogen spectral lines should attract our attention particularly."[20] Balmer noticed that the wavelengths of the four hydrogen lines as measured by Ångström could be represented in terms of a "basic number" $h = 3645.6 \times 10^{-7}$ as $\frac{9}{5}h$, $\frac{4}{3}h$, $\frac{25}{21}h$, and $\frac{9}{8}h$ or, equivalently, as $\frac{9}{5}h$, $\frac{16}{12}h$, $\frac{25}{21}h$, and $\frac{36}{32}h$. He thus saw that the numerators form the sequence 3^2, 4^2, 5^2, 6^2 whereas the corresponding denominators are the differences of

[15] G. D. Liveing and J. Dewar, "On the spectra of sodium and potassium," *Proceedings of the Royal Society of London* (*A*), *29*, 398–402 (1879); reprinted in G. D. Liveing and J. Dewar, *Collected Papers on Spectroscopy* (Cambridge University Press, 1915), pp. 66–70.

[16] G. D. Liveing and J. Dewar, "The spectrum of magnesium," *Proceedings of the Royal Society of London* (*A*), *32*, 189–203 (1881); *Collected Papers on Spectroscopy* (REF. 15), pp. 118–132.

[17] A. Schuster, "On harmonic ratios in the spectra of gases," *Proceedings of the Royal Society of London* (*A*) *31*, 337–347 (1881).

[18] A. Schuster, "The genesis of spectra," *British Association Reports, Southhampton*, pp. 120–143 (1882).

[19] G. P. Thomson reports that when visiting Switzerland shortly after World War I, he was told by a young relative of J. J. Balmer that the latter (his great-uncle?) was a devotee of numerology, interested in such things as the number of the beast or the number of the steps of the pyramid. One day, chatting with a friend who happened to be a physicist or chemist, Balmer complained that he had "run out of things to do." Whereupon the friend replied: "Well, you are interested in numbers, why don't you see what you can make of this set of numbers that come from the spectrum of hydrogen?" and he gave him the wavelengths of the first few lines of the hydrogen spectrum. *Archive for the History of Quantum Physics*, Interview with G. P. Thomson on June 20, 1963.

[20] J. J. Balmer, "Notiz über die Spectrallinien des Wasserstoffs," *Verhandlungen der Naturforschenden Gesellschaft in Basel* *7*, 548–560 (1885).

squares $3^2 - 2^2$, $4^2 - 2^2$, $5^2 - 2^2$, $6^2 - 2^2$. He therefore expressed the wavelengths of these lines by the formula

$$\lambda = h \frac{m^2}{m^2 - 2^2} \quad \text{mm} \qquad (2.1)$$

where $h = 3645.6 \times 10^{-7}$ and $m = 3, 4, 5, 6$. Balmer also predicted the existence of a fifth line with wavelength 3969.65×10^{-7} mm. Informed by von Hagenbach that this line and other additional lines had indeed been discovered by Huggins, Balmer showed in a second paper[21] that his formula applied to all twelve then known hydrogen lines. He also predicted correctly that in the series which subsequently carried his name, no lines of wavelength longer than 6562×10^{-7} mm would ever be discovered and that the series would converge at 3645.6×10^{-7} mm. The agreement between the calculated and the observed values of the wavelengths was extremely close in the visible region, but for shorter wavelengths slight systematic discrepancies were evident. In view of these discrepancies Balmer expressed some doubts whether the fault lay with the formula or with the data.

Balmer's discovery had immediate repercussions and gave new impetus to a most intensive search for other regularities in spectra. In an address delivered before the British Association for the Advancement of Science held in Bath in 1888, Runge[22] announced that in certain spectra he had discovered a number of harmonic series of lines whose wavelengths conform to formulas of the type

$$\frac{1}{\lambda} = a + \frac{b}{m} + \frac{c}{m^2} \qquad \text{or} \qquad \frac{1}{\lambda} = a' + \frac{b'}{m^2} + \frac{c'}{m^4}$$

where a, b, c, a', b', c' are constants and m is an integer. Balmer's formula (2.1), he pointed out, was a special case of the first type mentioned, namely, when $a = h^{-1}$, $b = 0$, and $c = -4h^{-1}$. In a detailed study on the structure of emission spectra, published in the *Transactions of the Royal Swedish Academy* in 1890, Rydberg[23] claimed he had been using Balmer's formula long before its publication. Stating as a fundamental principle that "in the spectra of all the elements analyzed so far there are series of rays whose wavelengths or wave numbers are functions of consecutive

[21] J. J. Balmer, "Zweite Notiz über die Spectrallinien des Wasserstoffs," *ibid.*, 750–752 (1885); *Wiedemannsche Annalen der Physik 25*, 80–87 (1885).

[22] C. Runge, "On the harmonic series of lines in the spectra of the elements," *British Association Reports, Bath*, pp. 576–577 (1888).

[23] J. R. Rydberg, "Recherches sur la constitution des spectres d'émission des éléments chimiques," *Kungliga Vetenskaps Akademiens Handlingar 23*, no. 11, 155 pp. (1890). Cf. also J. R. Rydberg, "On the structure of the line-spectra of the chemical elements," *Philosophical Magazine 29*, 331–337 (1890); "Sur la constitution des spectres linéaires des éléments chimiques," *Comptes Rendus 110*, 394–397 (1890); "Ueber den Bau der Linienspectren der chemischen Grundstoffe," *Zeitschrift für Physikalische Chemie 5*, 227–232 (1890).

integral numbers,"[24] Rydberg expressed these functions by a general formula $n = n_0 - N_0/(m + \mu)^2$, where n was the wave number ["nombre des longueurs d'onde sur l'unité de longueur (1 cm)"], n_0 and μ constants for each series, and N_0, later called "Rydberg's constant" and denoted by R, a constant common to all series and to all elements. Having shown that Balmer's formula was a special case with $n_0 = h^{-1}$, $N_0 = 4h^{-1}$, and $\mu = 0$, Rydberg calculated, on the basis of Ångström's measurements of the first four hydrogen lines, the value of N_0 as 109721.6 cm^{-1}.

Referring to the discoveries of Liveing and Dewar, who identified the principal, sharp ("second subordinate series") and diffuse ("first subordinate series") series in the spectra of the alkali metals, and to the work of Hartley,[25] who observed recurrent frequency differences for the components of certain doublet and triplet series ("Hartley's Law"), Rydberg showed that the wave numbers of the lines in these series can be expressed as functions of an integer m as follows: the component with the longer wavelength in each doublet of the principal series could be expressed by $n = n_0 - N_0/(m + p_1)^2$ and the other component by $n = n_0 - N_0/(m + p_2)^2$; correspondingly, the two components of each line in the first subordinate series could be expressed by $n = n_0' - N_0/(m + d)^2$ and $n = n_0'' - N_0/(m + d)^2$, and those of the second subordinate series by $n = n_0' - N_0/(m + s)^2$ and $n = n_0'' - N_0/(m + s)^2$. In 1896 Rydberg[26] and (independently) Schuster[27] discovered that the difference between the limit of the principal series and the common limit of the two other series coincided with the wave number of the first line of the principal series, that is, that the limits n_0' and n_0'' of the subordinate series coincided with $N_0/(2 + p_2)^2$ and $N_0/(2 + p_1)^2$, and, similarly, that the limit of the principal series coincided with $N_0/(1 + s)^2$. The series were therefore represented by the formulas

$$n = \frac{N_0}{(1 + s)^2} - \frac{N_0}{(m + p)^2}$$

with $p = p_1$ or p_2 and $m = 2, 3, \ldots$ for the two components of the principal series,

$$n = \frac{N_0}{(2 + p_2)^2} - \frac{N_0}{(m + d)^2} \qquad \text{and} \qquad n = \frac{N_0}{(2 + p_1)^2} - \frac{N_0}{(m + d)^2}$$

[24] "Dans les spectres de tous les éléments analysés il y a des séries de raies dont les longueurs d'onde sont des fonctions déterminées des nombres entiers consécutifs." *Ibid.* ("Recherches"), p. 33.

[25] W. N. Hartley, "On homologous spectra," *Journal of the Chemical Society 43*, 390–400 (1883).

[26] J. R. Rydberg, "Die neuen Grundstoffe des Cleveitgases," *Wiedemannsche Annalen der Physik 58*, 674–679 (1896).

[27] A. Schuster, "On a new law connecting the periods of molecular vibrations," *Nature 55*, 200–201 (1897); the article was written in 1896.

with $m = 3, 4, \ldots$ for those of the diffuse series, and finally

$$n = \frac{N_0}{(2 + p_2)^2} - \frac{N_0}{(m + s)^2} \quad \text{and} \quad n = \frac{N_0}{(2 + p_1)^2} - \frac{N_0}{(m + s)^2}$$

with $m = 2, 3, \ldots$ for those components of the sharp series. In 1907 Bergmann[28] found in the infrared spectra of potassium, rubidium, and cesium a fourth series whose convergence limit coincided with $N_0/(3 + d)^2$ and whose wave numbers were expressed by

$$n = \frac{N_0}{(3 + d)^2} - \frac{N_0}{(m + f)^2}$$

where $m = 4, 5, \ldots$. Some of the lines of this series, which was later called the "fundamental series" or "Bergmann series," had been discovered previously by Saunders.[29]

It occurred to Rydberg[30] and was later explicitly stated as a fundamental principle by Ritz[31] that the frequency of every spectral line of an element could be expressed as the difference between two terms or "spectral terms," each of which contained an integer. Ritz's principle, or, as it was subsequently called, "the combination principle," could not be accounted for by classical physics. In order to understand the reason for this incompatibility, it must be noted that the above-mentioned hypothesis according to which the spectrum as a whole was thought to be produced by the free vibrations of one single atom had meanwhile been refuted. For Conway[32] showed convincingly, in 1907, that each atom could give rise to only one spectral line at a time. Conway's contention was further elaborated by Bevan's[33] analysis of the anomalous dispersion by potassium vapor. Bevan showed that any theoretical explanation of this phenomenon, if worked out on the basis of the previous hypothesis, would necessarily imply an excessively great number of electrons per molecule. Each individual line in a spectrum had therefore to be associated with the periodic motion of an electron and the different lines of the spectrum with motions of excited electrons in different atoms. Classically, the spectrum of light

[28] A. Bergmann, *Beiträge zur Kenntnis der ultraroten Emissionsspektren der Alkalien*, Dissertation, Jena, 1907.

[29] F. A. Saunders, "Some additions to the arc spectra of the alkali metals," *Astrophysical Journal 20*, 188–201 (1904).

[30] J. R. Rydberg, "La distribution des raies spectrales," in *Rapports présentés au Congrès International de Physique* (Gauthier-Villars, Paris, 1900), vol. 2, pp. 200–224.

[31] W. Ritz, "Über ein neues Gesetz der Serienspektren," *Physikalische Zeitschrift 9*, 521–529 (1908); "On a new law of series spectra," *Astrophysical Journal 28*, 237–243 (1908). "Durch additive oder subtraktive Kombination, sei es der Serienformeln selbst, sei es der in dieselben eingehenden Konstanten, werden Formeln gebildet, die gewiße neu entdeckte Linien vollständig aus den früher bekannten zu berechnen gestatten." *Gesammelte Werke* (Gauthier-Villars, Paris, 1911), p. 162.

[32] A. W. Conway, "On series spectra," *Scientific Proceedings of the Royal Dublin Society 11*, 181–183 (1907).

[33] P. V. Bevan, "Dispersion of light by potassium vapour," *Proceedings of the Royal Society of London* (A), *84*, 209–225 (1910).

had consequently to contain, together with the fundamental vibration, the higher harmonics whose frequencies have the form of a sum of integral multiples of the fundamental frequencies, a result inconsistent with Ritz's combination principle. We thus see that the study of the discrete spectra, like that of the continuous spectra, led to serious inconsistencies with classical physics.

2.2 Bohr's Theory of the Hydrogen Atom

Our preceding remarks on spectroscopy were confined to merely tracing the origin and early development of the combination principle. Other aspects of spectroscopic research and their influence on the conceptual development of quantum theory will be discussed in a different context. At present, it should be noted that the vast amount of work invested in the search for numerical relations among spectral lines was motivated by the hope that these relations, by analogy to certain problems in the theory of mechanical and acoustical vibrations, would throw new light upon the nature of the proper oscillations of the atom or its electrons and thus lead to an understanding of atomic structure and of microscopic processes. The combination principle, however, revealed the futility of such an approach. It gradually became clear that the establishment of merely mathematical relations devoid of any consistent theory would be labor in vain. The only way to avoid this impasse, it seemed, was to take refuge in a model of the atom whose structure could be based on independent evidence from other sources and to apply the mathematical relations to the model. The outcome of this conceptual development was, of course, Niels Bohr's synthesis of the combination principle with Rutherford's atómic model on the basis of Planck's quantum conception.

In fact, Bohr's work itself was intimately connected with the problem of finding a consistent model of the atom. Even external circumstances of his life were connected with it. For when Bohr left J. J. Thomson's laboratory in Cambridge, in March, 1912, to join Rutherford's team in Manchester, it was because of a disagreement with Thomson concerning the latter's "plum-cake" model of the atom—or, as Condon once phrased it, because "J. J. politely indicated that it might be nice if he [Bohr] left Cambridge and went to work with Rutherford."[34] It was a fortunate turn of fate, not only with respect to the outcome when eventually Bohr's brilliant and successful theory of the hydrogen atom contributed decidedly to the general acceptance of the Rutherford model, but also with respect to the whole time of Bohr's stay in Manchester; for there he found sympa-

[34] E. U. Condon, "60 years of quantum mechanics," *Physics Today 15*, 45 (1962).

thetic understanding and even encouragement from the very beginning of his work. More than fifteen years later Rutherford recollected: "On my side, the agreement with Planck's deduction of e early made me an adherent to the general idea of a quantum of action. I was in consequence able to view with equanimity and even to encourage Prof. Bohr's bold application of the quantum theory to explain the origin of spectra."[35]

For a full comprehension of Bohr's work we shall have to discuss briefly the development of atomic models at that time.

Nineteenth-century models of the atom, such as those proposed by Kelvin, Helmholtz, or Bjerknes, were primarily mechanical or hydrodynamical and were invalidated by the discovery of electrons and radioactive disintegration. One of the earliest models consistent with these discoveries was proposed by Perrin[36] in a popular lecture delivered to students and friends of the Sorbonne in 1901. It consisted of a positively charged particle surrounded by a number of electrons ("sorte de petites planètes") compensating the central charge. Perrin assumed that the internal electromagnetic forces could produce a dynamically stable system whose rotational periods would correspond to the frequencies or wavelengths of the lines in the emission spectrum of the atom.

Two years later, in December, 1903, J. J. Thomson[37] developed the atomic model to which reference was made in the preceding chapter. The hydrogen atom, for example, was represented by a positively charged sphere of a radius of about 10^{-8} cm with an electron oscillating at its center. Thomson's model had one great advantage: it implied without any additional assumptions a quasi-elastic binding of the electrons, a property which had been a basic hypothesis for Drude, Voigt, Planck, and Lorentz in their work on dispersion, absorption, and other phenomena. In particular, it was a convenient assumption for the explanation of monochromatic spectral lines whose frequencies were independent of the energy of vibration.

Thomson's model, however, failed to account for the large angle

[35] Note by Prof. E. Rutherford, *Die Naturwissenschaften 17*, 483 (1929). On Planck's calculation of the elementary charge e see p. 21.

[36] J. Perrin, "Les hypothèses moléculaires," *Revue Scientifique 15*, 449–461 (1901); reprinted in Jean Baptiste Perrin, *Œuvres Scientifiques* (Centre National de la Recherche Scientifique, Paris, 1950).

[37] J. J. Thomson, "The magnetic properties of systems of corpuscles describing circular orbits," *Philosophical Magazine 6*, 673–693 (1903); his main paper on this subject appeared in 1904: "On the structure of the atom—an investigation of the stability and periods of oscillation of a number of corpuscles arranged at equal intervals around the circumference of a circle; with application of the results to the theory of atomic structure," *ibid. 7*, 237–265 (1904). At the same time (1903) Philipp Lenard, experimenting on the penetration of cathode-ray particles through matter, suggested a model according to which the atom is built up of "dynamides," electric doublets, possessing mass, but of so small a magnitude ($\sim 10^{-12}$ cm) that only a vanishingly small part of the atomic volume is not empty. Cf. P. Lenard, "Über die Absorption von Kathodenstrahlen verschiedener Geschwindigkeit," *Annalen der Physik 12*, 714–744 (1903).

deflections, up to 150° with reference to the incident direction, in the scattering experiments with α particles which were carried out a few years later by Thomson's students, Geiger and Marsden.[38] When Thomson's explanations of these results on the basis of multiple scattering proved untenable,[39] Rutherford's theory of "single scattering"[40] and his well-known model of the atom became firmly established. Thomson's model also failed to explain the subsequently (1913) discovered Stark effect, which will be discussed later on. Finally—but this, of course, was not known until much later—if the Thomson model is quantized,[41] the resulting energy states, although almost identical with those of the Rutherford model, turn out to be generally nondegenerate. Thus, even had no Rutherford scattering experiments ever been performed, spectroscopic evidence alone would have decided in favor of the Rutherford model.

At the time when Thomson developed his atomic model, the Japanese physicist Nagaoka,[42] in an address before the Physico-Mathematical Society of Tokyo in December, 1903, proposed what he called a "Saturnian model." It consisted, like Perrin's, of a positively charged central particle surrounded by a number of equidistant electrons revolving with a common angular velocity. Nagaoka then tried to show that the lines in the emission spectrum have their origin in small transversal oscillations of the electron configuration. Referring to the treatment of similar oscillations in Maxwell's essay "On the stability of the motion of Saturn's rings,"[43] Nagaoka claimed he had proved the dynamical stability of his model and its compatibility with the spectroscopic observations of Runge and Rydberg. The correctness

[38] H. Geiger and E. Marsden, "On a diffuse reflection of the α-particles," *Proceedings of the Royal Society (A)*,*82*,495–500 (1909); "The scattering of α-particles by matter," *ibid. 83*, 492–504 (1910).

[39] An analysis of the Thomson scattering leads to a probability formula with an exponential dependence on the angle of deflection φ, in disagreement with the observed $\sin^{-4}(\varphi/2)$ angle dependence. For details cf. G. P. Harnwell and W. E. Stephens, *Atomic Physics* (McGraw-Hill, New York, 1955), pp. 99–108.

[40] E. Rutherford, "The scattering of α and β particles by matter and the structure of the atom," *Philosophical Magazine 21*, 669–688 (1911); *The Collected Papers of Lord Rutherford of Nelson* (Interscience, New York, 1962), vol. 2, pp. 238–254; "The structure of the atom," *Philosophical Magazine 27*, 488–498 (1914); *Collected Papers*, vol. 2, pp. 445–455. The former paper, which already contained his famous scattering formula, has been reprinted in R. T. Beyer (ed.), *Foundations of Nuclear Physics* (Dover, New York, 1949), pp. 111–130, and in J. B. Birks (ed.), *Rutherford at Manchester* (Heywood, London, 1962; W. A. Benjamin, New York, 1963), pp. 182–204.

[41] Such a quantization has been performed by H. Zatzkis in his paper "Thomson atom," *American Journal of Physics 26*, 635–638 (1958).

[42] H. Nagaoka, "Motion of particles in an ideal atom illustrating the line and band spectra and the phenomena of radioactivity," *Bulletin of the Mathematical and Physical Society of Tokyo 2*, 140–141 (1904); "On a dynamical system illustrating the spectrum lines and the phenomena of radio-activity," *Nature* 69, 392–393 (1904); "Kinetics of a system of particles illustrating the line and band spectrum and the phenomena of radioactivity," *Philosophical Magazine 7*, 445–455 (1904).

[43] J. C. Maxwell, *Scientific Papers* (REF. 56 OF CHAP. 1), vol. 1, pp. 288–376.

of these computations and, in particular, the stability of the model, however, were soon challenged by Schott.[44]

Perrin's and Nagaoka's atomic models were further elaborated by the Cambridge astrophysicist Nicholson[45] in an attempt to explain the nature of a number of unidentified lines in the spectra of nebulae and in the spectrum of the solar corona. Associating these lines with the hypothetical elements "nebulium" and "protofluorine," Nicholson, closely following Nagaoka's suggestion, constructed atomic models to account for these lines. On the assumption of a central charge of four units surrounded by four electrons, Nicholson showed that the ratio between the frequencies corresponding to two different vibrational modes of the electronic ring coincided with the ratio between the frequencies of two lines in the nebular spectrum. This agreement, in his view, constituted sufficient evidence for the adequacy of his model. Nicholson then proceeded to give detailed calculations for other lines and to develop a general theory, in the course of which he made a number of important discoveries. His theory appeared to him to have been given even observational support. For the frequency of a third mode (λ4353), which he computed as a sequel to the two modes mentioned before and which, at the time of his first publication, was not known to correspond to any known spectral line, had actually been observed by W. H. Wright at the Lick Observatory and by M. Wolf at the Heidelberg Observatory.[46] Only in 1927 was the nature of the "nebulium" lines definitely clarified when Bowen showed that they are forbidden lines of highly ionized oxygen and nitrogen (NII, OII, and OIII).[47]

With respect to his model of the atom, Nicholson declared that "the main conception involved . . . is that of the nature of positive electricity. This is supposed to exist in small spherical volume distributions of uniform density, whose radius is small in comparison even with that of the electron, a reversal of the more generally accepted view. The mass of these positive units is very large in comparison with that of an electron, and gives rise to nearly the whole mass of an atom. . . ."[48] In his third essay, published in June, 1912, Nicholson suggested relating the occurrence of spectral series to Planck's constant of action. "The quantum theory," he stated, "has apparently not been put forward as an explanation of 'series' spectra. . . . Yet, in the belief of the writer, it furnishes the true explanation in certain cases, and we are led to suppose that lines of a series may not emanate from

[44] G. A. Schott, "A dynamical system illustrating the spectrum lines and the phenomena of radio-activity," *Nature 69*, 437 (1904). "On the kinetics of a system of particles illustrating the line and band spectra," *Philosophical Magazine 8*, 384–387 (1904).

[45] J. W. Nicholson, "The spectrum of nebulium," *Monthly Notices of the Royal Astronomical Society 72*, 49–64 (1912); "The constitution of the solar corona," *ibid.*, 139–150, 677–693, 729–739.

[46] J. W. Nicholson, "On the new nebular line at λ4353," *ibid.*, 693.

[47] I. S. Bowen, "The origin of the nebulium lines," *Nature 120*, 473 (1927).

[48] REF. 45, p. 49.

the same atom, but from atoms whose internal angular momenta have, by radiation or otherwise, run down by various discrete amounts from a standard value."[49]

Nicholson incorporated Planck's quantum of action into his theory by contending that the frequencies of different observed spectral lines can be accounted for on the following assumption: that the ratio between the energy of the system and the frequency of rotation of the ring of electrons is given by an integral multiple of Planck's constant. Nicholson's theory, based as it was on a correspondence between the frequencies of optical and of mechanical vibrations, was, of course, by no means compatible with the Ritz combination principle. Nor was his introduction of Planck's constant motivated by any considerations concerning the stability of his atomic model. In fact, with the exception of his casual remark to the effect that "the electrons in steady motion must lie in one plane, in order that their energy may not be dissipated by rapid radiation,"[50] Nicholson completely ignored the stability problem.

It is a curious coincidence in the history of our subject that Nicholson's most important innovations, namely, his idea of a heavy nucleus and his conception of spectra as quantal phenomena, were actually obtained at the same time by independent research. For it was in May, 1911, that Ernest Rutherford refuted Thomson's hypothesis of multiple scattering and established his well-known model of the atom in accordance with the large angle deflections of α particles by single encounters.[51] It was also in 1911 that Bjerrum, following a suggestion by Nernst,[52] made the first successful application of the quantum principle to molecular spectra when he showed[53] that the quantization of the rotational energy of molecules accounted for certain features in the absorption spectra of gaseous hydrochloric and hydrobromic acids. It seems beyond doubt that neither Rutherford nor Bjerrum knew of Nicholson's ideas and that the latter's conjectures were in no way influenced by the former. It should also be noted that Nicholson's anticipations of some of Bohr's conclusions were based, as Rosenfeld has pointed out,[54] on a most questionable and often even fallacious reasoning.

Bohr's first research in Manchester on the absorption of α particles by matter,[55] which he finished in the summer of 1912, proved highly instructive for his future work. Treating the problem, which had been taken

[49] *Ibid.*, p. 729.

[50] *Ibid.*, p. 50.

[51] See REF. 40.

[52] W. Nernst, "Zur Theorie der spezifischen Wärme und über die Anwendung der Lehre von den Energiequanten auf physikalisch-chemische Fragen überhaupt," *Zeitschrift für Elektrochemie 17*, 265–275 (1911).

[53] N. Bjerrum, "Über die ultraroten Absorptionsspektren der Gase," in *Nernst-Festschrift*, 1912, pp. 90–98.

[54] Cf. L. Rosenfeld's introduction to Niels Bohr's *On the Constitution of Atoms and Molecules* (reprint of Bohr's papers of 1913; Munksgaard, Copenhagen, and W. A. Benjamin, New York, 1963), pp. xii-xiii.

[55] N. Bohr, "On the theory of the decrease of velocity of moving electrified particles on passing through matter," *Philosophical Magazine 25*, 10–31 (1913).

up in terms of classical mechanics by J. J. Thomson as early as 1906, long before the discovery of the atomic nucleus, Bohr assumed an elastic binding of the atomic electrons. This binding, although entering his calculations only through the periods of motions which Bohr inferred from the characteristic resonances as known from optical dispersion, played an essential role in limiting the effective region of energy transfer around the path of the penetrating particle. Associated now with Rutherford's atomic model, the binding of electrons and the concomitant problem of the stability of the atom had to engage Bohr's attention from the outset of his work. For Bohr saw not only the merits of Rutherford's model but also the difficulties which it raised and, in particular, the fact that, in contrast to Thomson's model, dynamical principles alone could not provide any scale for its size. In June, 1912, in the first draft of his classic paper "On the constitution of atoms and molecules,[56] Bohr wrote:[57] "In the investigation of the configuration of the electrons in the atoms we immediately meet with the difficulty . . . that a ring, if only the strength of the central charge and the number of electrons in the ring are given, can rotate with an infinitely great number of different times of rotation, according to the assumed different radius of the ring; and there seems to be nothing . . . to allow, from mechanical considerations to discriminate between the different radii and times of vibration. In the further investigation we shall therefore introduce and make use of a hypothesis, from which we can determine the quantities in question. This hypothesis is: that for any stable ring (any ring occurring in the natural atoms) there will be a definite ratio between the kinetic energy of an electron in the ring and the time of rotation.[58] This hypothesis, for which no attempt at a mechanical foundation will be given (as it seems hopeless), is chosen as the only one which seems to offer a possibility of an explanation of the whole group of experimental results, which gather about and seems to confirm conceptions of the mechanismus of the radiation as the ones proposed by Planck and Einstein." This draft, composed of six manuscript sheets (one of which is unfortunately lost), was written by Bohr as a private communication to Rutherford and is naturally an important document for the understanding of the conceptual development of Bohr's atomic theory. Bohr realized that the stability of the Rutherford model could by no means be reconciled with the principles of Newton's mechanics and Maxwell's electrodynamics. For no system of point charges, according to these principles, ever admits of a stable equilibrium, and any dynamical equilibrium, based on the motions

[56] *Philosophical Magazine 26*, 1–25, 476–502, 857–875 (1913). For a recent reprint cf. REF. 54. German translation in N. Bohr, *Abhandlungen über Atombau aus den Jahren 1913–1916*, translated by H. Stintzing (Friedr. Vieweg, Braunschweig, 1921); reprinted in *Dokumente der Naturwissenschaft—Abteilung Physik* (Ernst Battenberg Verlag, Stuttgart, 1964), vol. 5, pp. 33–57, 58–83, 84–101.

[57] REF. 54, p. xxiii.

[58] Bohr obviously meant "angular velocity" instead of "time of rotation."

of electrons, must lead to a radiative dissipation of energy accompanied by a steady contraction of the system.

Since in Planck's discovery a fundamental limitation of classical physics had already been revealed, Bohr argued that the answer to the stability problem had to be sought in Planck's quantum of action. In contrast to his predecessors who related Planck's h to atomic models with the purpose of finding a mechanical or electromagnetic interpretation of h, Bohr recognized that Planck's constant should be applied to Rutherford's model not in order to elucidate the physical significance of the former, but rather to account for the stability of the latter. Bohr realized that to this end the theory should yield a constant of the dimension of length, characterizing the distance of the electron from the center of the stable orbit. But the only constant parameters that appeared in Rutherford's model of the atom were those of masses and charges, and from these no constant of the dimension of length could possibly be formed. In the fact, however, that the adjunction of h to m and e made it possible to construct an expression, such as h^2/me^2, which has the dimension of length—even with the required order of magnitude ($\approx 20 \times 10^{-8}$ cm)—Bohr saw additional evidence for the correctness of his assumption.

All previous applications of Planck's constant to atomic models referred to the Thomson atom and were generally based on the assumption of harmonic oscillations for which the rule of quantization could be derived from Planck's work. The most noteworthy of these attempts was Haas's conjecture, to which reference has been made before.[59] In an attempt to interpret the photoelectric effect as a resonance phenomenon between orbital frequencies and the frequencies of the incident radiation, Lindemann,[60] in 1911, applied Kepler's laws to the assumedly elliptical orbits of the electrons but otherwise adhered to Thomson's model. In March, 1912, Herzfeld[61] proposed a modification of Thomson's model by assuming circular electronic orbits and a nonuniform charge density of the positive sphere and derived from these assumptions the Balmer series by a quantization of energy in accordance with a rule formulated by Hasenöhrl[62] as a generalization of Planck's prescription for the quantization of the harmonic oscillator. But all these and similar[63] calculations, although leading to an agreement as to the order of magnitude between the calculated and observed values for the frequencies and dimensions of the atoms, lost their

[59] See REF. 168 OF CHAP. 1.

[60] F. A. Lindemann, "Über die Berechnung der Eigenfrequenzen der Elektronen im selektiven Photoeffekt," *Vehandlungen der Deutschen Physikalischen Gesellschaft 13*, 482–488 (1911).

[61] K. F. Herzfeld, "Über ein Atommodell, das die Balmer'sche Wasserstoffserie aussendet," *Wiener Berichte 121*, 593–601 (1912).

[62] F. Hasenöhrl, "Über die Grundlagen der mechanischen Theorie der Wärme," *Physikalische Zeitschrift 12*, 931–935 (1911).

[63] E. Wertheimer, "Zur Haberschen Theorie der Wärmetönung," *Verhandlungen der Deutschen Physikalischen Gesellschaft 14*, 431–437 (1912).

validity with the abandonment of the Thomson model on which they were based. Nicholson's hypotheses, with which Bohr became acquainted only toward the end of 1912, as we know from a Christmas card[64] sent by him to his brother Harald, were similarly invalidated, although on other grounds.

The basic problem which Bohr had to face was the question of how to apply Planck's quantum of action to the Rutherford model of the atom. On the assumption that the hydrogen atom consists of an electron revolving around a nucleus whose charge is equal and opposite to that of the electron and whose mass is very large in comparison with the mass m of the electron, Bohr first investigated how far classical mechanics could be employed. From Kepler's first law he knew that the orbit of the electron is an ellipse with the nucleus in one of its foci. Calling the major axis of the orbit $2a$, and the energy which has to be added to the system in order to remove the electron to an infinite distance from the nucleus W, the charge of the electron e, and that of the nucleus e', Bohr could easily show that on the basis of classical principles

$$\omega = \frac{\sqrt{2}}{\pi}\frac{W^{3/2}}{ee'\sqrt{m}} \qquad 2a = \frac{ee'}{W} \tag{2.2}$$

which indicates that the frequency of revolution ω and the major axis of the orbit depend only on the value of W and are independent of the eccentricity of the orbit. In the special case of a circular orbit with radius a, a direct proof of Eq. (2.2) can readily be established. In this case, $mv^2/a = ee'/a^2$ (centripetal force = force of attraction) shows that the total energy $U = \frac{1}{2}mv^2 - ee'/a = -ee'/2a = -W$ or $W = ee'/2a$; and from $v = 2\pi\omega a$ the first part of Eq. (2.2) follows immediately. Bohr now saw that by varying W all possible values for ω and $2a$ could be obtained. The existence of sharp spectral lines, however, shows that the latter quantities have to assume definite values characteristic for the system. Moreover, as a simple consideration of the dimensions verifies, no combination of e, e', and m can yield a quantity with the dimension of length, a condition necessary for its interpretation as the diameter of the atom. So far, Bohr ignored the radiation of energy which according to Maxwell's theory should be dissipated at a rate proportional to the square of the acceleration of the electron. If this radiation were taken into consideration, W would steadily increase and with it the frequency of revolution ω while the dimensions of the orbit would continually decrease, producing a continuous spectrum instead of discrete spectral lines as observed. Thus the atom would be not only indeterminate in its dimensions but also deprived of any stability whatever. Realizing the incompatibility of ordinary mechanics and electrodynamics with Rutherford's atomic model and in direct contradiction to Newton's

[64] REF. 54, p. xxxvi.

mechanics and Maxwell's electrodynamics, Bohr boldly postulated the following assumption in order to endow the atom with size and stability. There exists a discrete set of permissible or *stationary* orbits; and as long as the electron remains in any stationary orbit, no energy is radiated. It is interesting to note that the second part of this assumption, though not explicitly formulated, had been used a few years earlier by Langevin[65] in his theory of permanent magnetism.

Although convinced that the discreteness of the orbits (or of a) and, according to Eq. (2.2), also of W and ω was somehow connected with Planck's constant of action, Bohr was unable to identify the exact relationship until February, 1913. Two apparently unrelated phenomena gave him the clue to the solution of the problem. He had been acquainted from his Cambridge days with Whiddington's experiments.[66] Whiddington had shown that when an anticathode was bombarded by cathode rays of increasing velocity, sudden changes in the nature of the emitted radiation were produced at certain critical velocities. It seems that Whiddington's work suggested to Bohr the idea of energy levels.[67] In fact, Whiddington's results, as, of course, became clear only later on, constituted in the field of x-rays one of the most striking verifications of Bohr's theory, just as the subsequent Franck-Hertz experiments did in the range of visible light. The other clue came from spectroscopy. Even by the end of January, 1913, Bohr was not fully aware of the implications of spectroscopic research for his problem. For in a letter dated January 31, 1913, addressed to Rutherford from Copenhagen, where Bohr had served since September, 1912, as an assistant to Knudsen, Bohr declared: "I do not at all deal with the question of calculation of the frequencies corresponding to the lines in the visible spectrum. I have only tried, on the basis of the simple hypothesis, which I used from the beginning, to discuss the constitution of the atoms and molecules in their 'permanent' state."[68] A few days later, however, the spectroscopist H. M. Hansen, who had just arrived in Copenhagen from Göttingen, where he had been working under Voigt on the inverse Zeeman effect of lithium, drew his attention to Rydberg's work on the classification of spectral lines, a subject in which Bohr had not previously been interested. Asked by Hansen how the new model of the atom could account for the regularities discovered by Rydberg and Ritz, Bohr acquainted himself with the subject and soon recognized its importance for his problem. "As soon as I saw Balmer's formula," he stated repeatedly,[69] "the whole thing was immediately clear to me."

[65] P. Langevin, "Sur la théorie du magnétisme," *Comptes Rendus 139*, 1204–1207 (1904).

[66] R. Whiddington, "The production of characteristic Röntgen radiation," *Proceedings of the Royal Society of London* (*A*), *85*, 323–332 (1911).

[67] Cf. *Archive for the History of Quantum Physics*, Interview with Niels Bohr on Oct. 31, 1962.

[68] The full text of the letter is published in REF. 54, pp. xxxvi–xxxvii.

[69] REF. 54, p. xxxix.

How, indeed, Balmer's formula suggested to Bohr a way of incorporating quantum conceptions into the Rutherford model of the hydrogen atom will now be explained. For this purpose we shall closely analyze Bohr's exposition of this issue as presented in his epoch-making paper.[70] Balmer's formula and its immediate generalization can most conveniently be expressed, as we have seen in connection with the work of Ritz and Rydberg, by the equation[71]

$$\nu = Rc\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right) \tag{2.3}$$

Bohr derived this formula in the first part[72] of the above-mentioned paper by three different methods. In his first derivation[73] he adopted the basic assumption of Planck's "second theory,"[74] according to which the amount of energy emitted by an atomic vibrator of frequency ν is $\tau h\nu$, τ being an integer, namely, the number of quanta emitted, each of frequency ν. Considering an electron at a great distance apart from the nucleus and "of no sensible velocity relative to the latter," Bohr studied the binding of this electron with the nucleus as a result of which the electron "has settled down in a stationary (circular) orbit around the nucleus" with orbital frequency ω. During this process, Bohr contended, a "homogeneous" (monochromatic) radiation is emitted of a frequency ν, equal to half the frequency of revolution of the electron in its final orbit—this relation suggesting itself in view of the fact that "the frequency of revolution of the electron at the beginning of the emission is 0." Thus, from

$$W = \frac{\tau}{2} h\omega$$

Bohr obtained by Eq. (2.2)

$$W = \frac{2\pi^2 me^2e'^2}{\tau^2h^2} \qquad \omega = \frac{4\pi^2 me^2e'^2}{\tau^3h^3} \qquad 2a = \frac{\tau^2h^2}{2\pi^2 mee'}$$

expressions which for $\tau = 1$, $|e| = |e'| = 4.7 \times 10^{-10}$, $e/m = 5.31 \times 10^{17}$, and $h = 6.5 \times 10^{-27}$ yield $W = 13$ eV, $\omega = 6.2 \times 10^{15}$ sec^{-1}, and $2a = 1.1 \times 10^{-8}$ cm in agreement with the empirical values of the ionization potential, the optical frequencies, and the linear dimensions of the hydrogen atom. If, as he found, the energy emitted by the formation of one of the stationary states is for the hydrogen atom

$$W = \frac{2\pi^2 me^4}{h^2\tau^2}$$

[70] REF. 56.
[71] Cf. REF. 23.
[72] REF. 56, pp. 1–25.
[73] *Ibid.*, pp. 5, 8, 9.
[74] REF. 195 OF CHAP. 1.

the "energy emitted by the passing of the system from a state corresponding to $\tau = \tau_1$ to one corresponding to $\tau = \tau_2$" turns out to be

$$W_{\tau_2} - W_{\tau_1} = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right)$$

Hence, since

$$W_{\tau_2} - W_{\tau_1} = h\nu$$

$$\nu = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right)$$

which is Balmer's formula.

In his second derivation[75] of the Balmer formula Bohr noted that it had not been necessary to assume that "a radiation is sent out corresponding to more than a single energy quantum $h\nu$." Since "as soon as one quantum is sent out the frequency is altered," it would be more consistent, he declared, to replace the previously assumed emission of τ quanta of frequency $\nu/2$ by that of one quantum of frequency $\tau\nu/2$. Bohr, in fact, generalized this relationship still further by putting the ratio between the emitted energy and the frequency of revolution of the electron for the different stationary states as

$$W = f(\tau)h\omega$$

where $f(\tau)$ is an as yet undetermined function of the integer τ. This he did because the particular choice $f(\tau) \equiv \tau/2$, as used in his first derivation, though plausible, did not seem to him to have sufficient logical cogency. Repeating now step by step the calculation of the first derivation, but with $\tau/2$ replaced by $f(\tau)$, Bohr obtained

$$\nu = \frac{\pi^2 me^2e'^2}{2h^3}\left[\frac{1}{f^2(\tau_2)} - \frac{1}{f^2(\tau_1)}\right]$$

Whereas in his first derivation the particular specification $f(\tau) \equiv \tau/2$ led him directly to the Balmer formula, he had now to pay for the greater generality of his assumption with an additional step: he had to take recourse to the structure of the Balmer formula itself in which the variable factor has the form $1/\tau_2^2 - 1/\tau_1^2$. To obtain such a factor he concluded that $f(\tau) = c\tau$. Here c is a constant which has to be determined. For this purpose he considered the transition of the system between two successive stationary states corresponding to $\tau = N$ and $\tau = N - 1$. By a simple calculation he obtained for the frequency of the radiation emitted

$$\nu = \frac{\pi^2 me^2e'^2}{2c^2h^3}\,\frac{2N - 1}{N^2(N - 1)^2}$$

[75] REF. 56, pp. 12, 13.

and for the frequencies of revolution of the electron before and after the emission

$$\omega_N = \frac{\pi^2 m e^2 e'^2}{2c^3 h^3 N^3} \qquad \omega_{N-1} = \frac{\pi^2 m e^2 e'^2}{2c^3 h^3 (N-1)^3}$$

"If N is great," Bohr continued, "the ratio between the frequency before and after the emission will be very nearly equal to 1; and according to ordinary electrodynamics we should therefore expect that the ratio between the frequency of radiation and the frequency of revolution also is very nearly equal to 1. This condition will only be satisfied if $c = \frac{1}{2}$." In fact, since

$$\frac{\nu}{\omega_N} = \frac{cN^3(2N-1)}{N^2(N-1)^2}$$

tends to $2c$ for large N, it approaches 1 only if $c = \frac{1}{2}$. Thus the result of the first derivation is retrieved.

In his third derivation[76] he dispensed altogether with Planck's relation by replacing it by what he called "an interpretation of the emission by analogy with ordinary electrodynamics." For, he declared, "an electron rotating round a nucleus in an elliptical orbit will emit a radiation which according to Fourier's theorem can be resolved into homogeneous components, the frequencies of which are $n\omega$, if ω is the frequency of revolution of the electron." Taking consequently the frequency of the energy emitted during the transition from a state in which no energy is yet emitted to another stationary state as equal to a multiple of $\omega/2$, where ω is the frequency of revolution of the electron in the state considered, Bohr arrived at the same expression as before. "Consequently," he declared in the conclusion of his present discussion, "we may regard our preliminary considerations . . . only as a simple form of representing the results of the theory."[77]

Bohr's approach, as we saw, was essentially an application of what he later termed the "correspondence principle," according to which, in the limit where the action involved is sufficiently large to permit the neglect of the individual quanta, the fundamentally statistical account of quantum phenomena can be represented as a rational generalization of the classical physical description. Bohr must have been aware that, by postulating the quantization of the angular momentum, he could have presented his theory in a mathematically more compact way. But distrusting the legitimacy of employing the conceptions of the "old mechanics" and avoiding their use whenever possible, Bohr rejected this alternative and gave greater credence to the application of the correspondence principle. In fact, when he wrote

[76] *Ibid.*, p. 14.

[77] *Ibid.*

the first part of his classic paper, the quantization of the angular momentum was for him merely an "interpretation" in terms of "symbols taken from ordinary mechanics." For he declared: "While there obviously can be no question of a mechanical foundation of the calculations given in this paper, it is, however, possible to give a very simple interpretation of the results of the calculations by help of symbols taken from ordinary mechanics. Denoting the angular momentum of the electron round the nucleus by M, we have immediately for a circular orbit $\pi M = T/\omega$, where ω is the frequency of revolution and T the kinetic energy of the electron; for a circular orbit we further have $T = W$, and from $W = \tau h\omega/2$ we consequently get $M = \tau M_0$, where $M_0 = h/2\pi = 1.04 \times 10^{-27}$. . . . The angular momentum of the electron round the nucleus in a stationary state of the system is equal to an entire multiple of a universal value, independent of the charge on the nucleus."[78] Clearly, in this case the quantization of the angular momentum and the formula $W = \frac{1}{2}\tau h\omega$ are mathematically equivalent statements. In the concluding remarks of his paper[79] Bohr summarized all his assumptions employed so far in the following formulation: "(1) That energy radiation is not emitted (or absorbed) in the continuous way assumed in the ordinary electrodynamics, but only during the passing of the systems between different 'stationary' states. (2) That the dynamical equilibrium of the systems in the stationary states is governed by the ordinary laws of mechanics, while these laws do not hold for the passing of the systems between the different stationary states. (3) That the radiation emitted during the transition of a system between two stationary states is homogeneous, and that the relation between the frequency ν and the total amount of energy emitted E is given by $E = h\nu$, where h is Planck's constant. (4) That the different stationary states of a simple system consisting of an electron rotating round a positive nucleus are determined by the condition that the ratio between the total energy, emitted during the formation of the configuration, and the frequency of revolution of the electron is an entire multiple of $\frac{1}{2}h$. Assuming that the orbit of the electron is circular, this assumption is equivalent with the assumption that the angular momentum of the electron round the nucleus is equal to an entire multiple of $h/2\pi$. (5) That the 'permanent' state of any atomic system, i.e., the state in which the energy emitted is maximum, is determined by the condition that the angular momentum of every electron round the centre of its orbit is equal to $h/2\pi$."

It should be noted in this context that Ehrenfest,[80] a short time prior

[78] *Ibid.*, p. 15.

[79] *Ibid.*, p. 874.

[80] P. Ehrenfest, "Bemerkung betreffs der spezifischen Wärme zweiatomiger Gase," *Verhandlungen der Deutschen Physikalischen Gesellschaft 15*, 451–457 (1913) (this paper appeared on June 15, 1913, whereas the first part of Bohr's paper appeared in the July issue of the *Philosophical Magazine*, 1913); *Collected Scientific Papers* (REF. 77 OF CHAP. 1), pp. 333–339.

to Bohr, had already applied the quantization of angular momentum without, however, formulating it as a general principle. This he did in his refinement of the Einstein-Stern theory (see REF. 104 OF CHAP. 1) of the specific heat of diatomic gases when he showed that the assumption $\frac{1}{2}L(2\pi\nu)^2 = nh\nu/2$ (L is the moment of inertia, ν the frequency, and n an integer) accounted for the empirical temperature dependence of the rotational energy of hydrogen without the need of introducing a zero-point energy.

In addition to the close agreement between the calculated and the observed values of the Rydberg constant, Bohr found support for the correctness of his theory in the fact that Eq. (2.3) applied not only to the Balmer series with $\tau_2 = 2$ but also for $\tau_2 = 3$ (and consequently $\tau_1 = 4, 5, \ldots$). The case $\tau_2 = 3$ corresponded to a series in the infrared which, after having already been predicted by Ritz,[81] was actually observed in 1908 by Paschen[82] and which was later called the "Paschen series." Moreover, Bohr's prediction that "if we put $\tau_2 = 1$ and $\tau_2 = 4, 5, \ldots$, we get series respectively in the extreme ultraviolet and extreme ultrared, which are not observed, but the existence of which may be expected"[83] was soon verified. The series for $\tau_2 = 1$ was observed by Lyman[84] in 1914, that for $\tau_2 = 4$ by Brackett[85] in 1922, and that for $\tau_2 = 5$ by Pfund[86] in 1924.

In 1913 it could be rightfully argued that the fact that not all lines predicted by Eq. (2.3) had actually been observed was an indication of the deficiency of experimental procedures rather than a disproof of Bohr's theory. The existence, however, of a single hydrogen line at variance with Eq. (2.3) would have shown that Bohr's theory was at least incomplete, if not altogether faulty. It was therefore a challenge to Bohr when his attention was drawn to a paper, published in 1896, in which the American astronomer Pickering claimed he had found hydrogen lines not accounted for by the ordinary Balmer formula in the spectrum of the star ζ Puppis. Nor did these lines, as it then became clear, agree with Bohr's more general formula (2.3). Pickering claimed having observed "a series of lines whose approximate wave-lengths are 3814, 3857, 3923, 4028, 4203, and 4505, the last line being very faint. These six lines," he argued, "form a rhythmical series like that of hydrogen and apparently are due to some element not yet found in other stars or on the Earth. The formula of Balmer will not represent this series, but if we add a constant term and write $\lambda = 4650[m^2/(m^2 - 4)] - 1032$, we obtain for m equal to 10, 9, 8, 7, 6 and 5 the wave-lengths 3812, 3858, 3928, 4031, 4199 and 4504."[87] One year later Pickering identified these lines as hydrogen lines for the following reason: "A remarkable relation exists between these two series, from which it appears that the second series, instead of being due to some unknown element as was at first supposed, is so closely allied to the hydrogen series, that it is probably due to that substance under conditions of temperature or pressure as yet unknown. The wave-length of the lines of hydrogen may be computed by the formula $3646.1[n^2/(n^2 - 16)]$ which is the formula of Balmer, slightly modifying the constant term so that the standard wave-length of Rowland shall be represented, and substituting $\frac{1}{2}n$ for m. The wave-length of the lines of hydrogen may be determined by this formula if we substitute for n the even integers 6, 8, 10, 12 etc. . . . If now we substitute for n the odd integers 5, 7, 9, 11 etc., we obtain the wave-lengths of the second series of lines in the spectrum of ζ Puppis."[88] Thus, one single formula, namely, $\lambda = 3646[n^2/(n^2 - 16)]$, applied both to the Balmer lines (for even n) and to the newly discovered lines (for odd n). Kayser[89] at first expressed some doubts about Pickering's identification of these lines but later[90] accepted the theory on the grounds that hydrogen would have two series, which "then corresponds admirably with the other elements." Kayser also pointed out: "That this series has never been observed before, can perhaps be explained by not sufficient temperatures in our Geissler tubes and most of the stars." When in July, 1897, the line $\lambda 5413.9$, corresponding to $n = 7$, also was observed as "clearly visible" in the spectrum of ζ Puppis,[91] Pickering's contentions were generally accepted.

Rydberg,[92] in accordance with his general classification of series, interpreted Balmer's series as the diffuse (or first subordinate) and Pickering's as the sharp (or second subordinate) series of hydrogen, so that the former corresponded to $n = n_0 - N_0/(m + 1)^2$ for $m = 2, 3, \ldots$ and the latter to $n = n_0 - N_0/(m + 0.5)^2$. Now, in accordance with the Rydberg-Schuster law a "principal series" of hydrogen should exist whose wave numbers are given by

$$n = \frac{N_0}{(1 + 0.5)^2} - \frac{N_0}{(m + 1)^2}$$

with $m = 1, 2, \ldots$, and whose first[93] member consequently is $\lambda 4687.88$. In fact, a line $\lambda 4686$ was actually observed[94] in the spectrum of ζ Puppis and

[81] W. Ritz, "Über ein neues Gesetz der Serienspektren," *Physikalische Zeitschrift 9*, 521–529 (1908).

[82] F. Paschen, "Zur Kenntnis ultra-roter Linienspektren," *Annalen der Physik 27*, 537–570 (1908).

[83] REF. 56, p. 9.

[84] T. Lyman, "An extension of the spectrum in the extreme-violet," *Physical Review 3*, 504–505 (1914).

[85] F. Brackett, "A new series of spectrum lines," *Nature 109*, 209 (1922).

[86] A. H. Pfund, "The emission of nitrogen and hydrogen in the infrared," *Journal of the Optical Society of America 9*, 193–196 (1924).

[87] E. C. Pickering, "Stars having peculiar spectra," *Astrophysical Journal 4*, 369–370 (1896). Cf. also *ibid.*, 142–143.

[88] E. C. Pickering, "The spectrum of ζ Puppis," *Astrophysical Journal 5*, 92–94 (1897).

[89] H. Kayser, "On the spectrum of ζ Puppis," *ibid.*, 95–97.

[90] H. Kayser, "On the spectrum of hydrogen," *ibid.*, 243.

[91] E. C. Pickering, "The spectrum of ζ Puppis," *ibid. 6*, 259 (1897).

[92] J. R. Rydberg, "The new series in the spectrum of hydrogen," *ibid. 6*, 233–238 (1897), *7*, 233 (1899).

[93] Owing to atmospheric absorption, the other lines $\lambda 2734.55$, $\lambda 2386.50$, . . . would not be visible.

[94] Cf. the footnote to Rydberg's paper (REF. 92) by Hale and Keeler.

also, during the Indian solar eclipse of January 22, 1898, in the spectrum of the sun's chromosphere.[95] Furthermore, in 1912 Fowler observed in the spectrum of a Plücker discharge tube containing a mixture of hydrogen and helium four lines at positions corresponding to Rydberg's so-called "principal series of hydrogen" and a new series of lines in the ultraviolet with the same high-frequency limit.[96]

These were the facts which Bohr then had to explain on the basis of his theory. At first he showed that the Pickering series and the hypothetical "principal series of hydrogen," originally expressed by

$$\nu = cR\left(\frac{1}{2^2} - \frac{1}{(m + \frac{1}{2})^2}\right) \quad \text{and} \quad \nu = cR\left(\frac{1}{1.5^2} - \frac{1}{m^2}\right)$$

with $m = 2, 3, \ldots$ respectively, could be rewritten as

$$\nu = 4cR\left(\frac{1}{4^2} - \frac{1}{k^2}\right)$$

with $k = 5, 7, \ldots$, and

$$\nu = 4cR\left(\frac{1}{3^2} - \frac{1}{k^2}\right)$$

with $k = 4, 6, \ldots$ respectively, that is, as series whose Rydberg constant is four times that of hydrogen. Bohr could now easily show that his theory, if applied to the ionized helium atom with nuclear charge $2e$, leads exactly to these formulas.

In a letter to Rutherford, dated March 6, 1913, Bohr referred to these ideas and wrote that "the chemist Dr. Bjerrum suggested to me that if my point was right the lines might also appear in a tube filled with a mixture of helium and chlorine (oxygen, or other electro-negative substances); indeed it was suggested, that the lines might be still stronger in this case. Now, we have not in Copenhagen the opportunity to do such an experiment satisfactorily; I might therefore ask you, if you possibly would let it perform in your laboratory, or if you perhaps kindly would forward the suggestion to Mr. Fowler, which may have the arrangement still standing."[97] In fact, when Evans,[98] following this suggestion, published a short note in *Nature* in which he indicated that his experiments did support Bohr's claim that helium, and not hydrogen, is the origin of the lines in

[95] Sir Norman Lockyer, Chisholm-Batten, and A. Pedler, "Total eclipse of the sun, January 22, 1898," *Philosophical Transactions of the Royal Society of London 197*, 151–228 (1901).

[96] A. Fowler, "Observations of the principal and other series of lines in the spectrum of hydrogen," *Monthly Notices of the Royal Astronomical Society 73*, 62–71 (1912). Small discrepancies between observed and calculated frequencies were noted. Their explanation was later supplied by the correction of the Rydberg constant for finite mass of the nucleus.

[97] REF. 54, p. xxxix.

[98] E. J. Evans, "The spectra of helium and hydrogen," *Nature 92*, 5 (Sept. 4, 1913).

question, Fowler[99] argued against Evans that the observed wavelengths of these lines differ, though only by a small amount, from their theoretical values. Bohr,[100] however, soon pointed out that if the finite ratio between the mass m of the electron and the mass m_n of the nucleus is taken into consideration, and if therefore the value of m in his formula for the Rydberg constant R is replaced by that of the "reduced mass"

$$m' = \frac{m}{1 + m/m_n}$$

the observed discrepancies of about 0.04 percent are fully accounted for. When subsequent experiments carried out by Evans[101] at the University of Manchester, by Fowler,[102] and by Paschen[103] corroborated this contention, Fowler's original objection became another striking confirmation of Bohr's theory.

It will also be recalled that the dependence of R on m_n, as contended by Bohr, led Urey[104] and his collaborators in 1932 to the discovery of heavy hydrogen or deuterium H^2 with an isotope shift of 1.79 Å for the first Balmer line H_α and 1.32 Å for H_β.

The most direct confirmation of Bohr's interpretation of spectral terms as stationary energy levels and of his frequency condition (assumptions 1 and 3 of his summary) was afforded by a series of experiments performed by Franck and Hertz.[105] Electrons from a thermoionic source were accelerated to a known energy and directed against atoms of a gas or vapor at low pressure. At low electronic energies only elastic collisions occurred and no radiation was observed. As soon, however, as the electron's energy was equal to or exceeded a critical value (4.9 eV in the case of mercury vapor), inelastic collisions took place and radiation (λ2537, the mercury resonance line) was observed. The energy loss of the electron corresponded to the energy difference between the ground state and the excited state of the atom which, by transition to the ground state, re-emits this energy in the form of light in accordance with Bohr's frequency condition.

[99] A. Fowler, "The spectra of helium and hydrogen," *ibid.*, 95 (Sept. 25, 1913).

[100] N. Bohr, "The spectra of helium and hydrogen," *ibid.*, 231–232 (Oct. 23, 1913).

[101] E. J. Evans, "The spectra of helium and hydrogen," *Philosophical Magazine 29*, 284–297 (1915).

[102] A. Fowler, "Series lines in spark spectra," *Proceedings of the Royal Society of London (A)*, *90*, 426–430 (1914).

[103] F. Paschen, "Bohr's Helium Linien," *Annalen der Physik 50*, 901–940 (1916).

[104] H. C. Urey, F. G. Brickwedde, and G. M. Murphy, "A hydrogen isotope of mass 2 and its concentration," *Physical Review 40*, 1–15 (1932).

[105] J. Franck and G. Hertz, "Über Zusammenstöße zwischen Elektronen und den Molekülen des Quecksilberdampfes und die Ionisierungsspannung desselben," *Verhandlungen der Deutschen Physikalischen Gesellschaft 16*, 457–467 (1914); "Über Kinetik von Elektronen und Ionen in Gasen," *Physikalische Zeitschrift 17*, 409–416 (1916); "Die Bestätigung der Bohrschen Atomtheorie im optischen Spektrum durch Untersuchungen der unelastischen Zusammenstöße langsamer Elektronen mit Gasmolekülen," *ibid. 20*, 132–143 (1919).

Our analysis of Bohr's contribution of 1913 would not do justice to his work if it confined itself to an exposition of the physical contents without due consideration of its philosophical foundations. First let us note that Bohr's theory was, in general, very favorably accepted. When Einstein, a severe censor as far as physical theoretizing was concerned, was informed in September, 1913, by Hevesy in Vienna that Evans's experiments had confirmed Bohr's ascription of the Pickering lines to helium, he described Bohr's theory as an "enormous achievement" and as "one of the greatest discoveries." In fact, Einstein recognized the importance of Bohr's theory as soon as he became acquainted with it. This happened when, in one of the weekly physics colloquia held in Zurich conjointly by the University and the Institute of Technology, a report on the first part of Bohr's 1913 paper was given shortly after its publication. At the end of the discussion von Laue protested: "This is all nonsense! Maxwell's equations are valid under all circumstances."[106] Whereupon Einstein rose and declared: "Very remarkable! There must be something behind it. I do not believe that the derivation of the absolute value of the Rydberg constant is purely fortuitous."[107]

Also in September, 1913, at the 83d meeting of the British Association for the Advancement of Science, Jeans, in "the most important discussion of Section A, if not of the whole meeting,"[108] gave a summarizing report on the subject of radiation.[109] Stating that "any discussion of the nature of radiation is of necessity inextricably involved in the larger question as to the ultimate form of the laws which govern the smallest processes of nature" and acknowledging the need for "a very extensive revision" of the laws which so far have been believed to be expressible in the form of differential equations, he spoke highly of Bohr's new theory. Although fully aware that this theory contains difficulties, still unsurmounted, "which appear to be enormous," such as the difficulty of explaining the Zeeman effect, Jeans regarded "the series of results obtained [by Bohr as] far too striking to be dismissed merely as accidental." He called Bohr's theory "a most ingenious and suggestive, and I think we must add convincing, explanation of the laws of spectral series."[110] The favorable acceptance of the new ideas was advanced by extremely good coverage of this meeting by the press and, in particular, by the report published in

[106] "Das ist Unsinn, die Maxwellschen Gleichungen gelten unter allen Umständen, ein Elektron auf Kreisbahn muß strahlen." For this quotation as well as the quotation in REF. 107 the author is indebted to Professor F. Tank (Zurich), who attended the colloquium (Letter of May 11, 1964, from Professor Tank to the author).

[107] "Sehr merkwürdig, da muß etwas dahinter sein; ich glaube nicht, daß die Rydbergkonstante durch Zufall in absoluten Werten ausgedrückt richtig herauskommt."

[108] "Physics at the British Association," *Nature 92*, 305 (1913).

[109] J. H. Jeans, "Discussion on Radiation," in *Report of the 83rd Meeting of the British Association for the Advancement of Science*, Birmingham, Sept. 10–17 (London, 1914), pp. 376–386.

[110] *Ibid.*, p. 376.

the Saturday issue of *The Times*[111] with its reference to "Dr. Bohr's ingenious explanation of the hydrogen spectrum," the article in *Nature*[112] which called Bohr's theory "convincing and brilliant," as well as Norman Campbell's résumé on the structure of the atom, also published in *Nature*,[113] which described Bohr's assumptions as "simple, plausible and easily amenable to mathematical treatment" and as leading to results "in exact quantitative agreement with observation."

Bohr himself, however, regarded his theory as merely a "preliminary and hypothetical" way of representing a number of experimental facts which defied all explanation on the basis of ordinary electrodynamics and classical mechanics. In an address delivered before the Physical Society in Copenhagen on December 20, 1913, Bohr[114] declared as his present objective not "to propose an explanation of the spectral laws" but rather "to indicate a way in which it appears possible to bring the spectral laws into close connection with other properties of the elements, which appear to be equally inexplicable on the basis of the present state of the science."[115] In fact, his intention was not to give a satisfactory answer to a definite question but to search for the right question to ask. For it was an established fact for him that ordinary electrodynamics and classical mechanics are inadequate to account for the stability of Rutherford's atomic model and that it is impossible "to obtain a satisfactory explanation of the experiments on temperature radiation with the aid of electrodynamics, no matter what atomic model be employed. The fact that the deficiencies of the atomic model we are considering stand out so plainly is therefore perhaps no serious drawback; even though the defects of other atomic models are much better concealed, they must nevertheless be present and will be just as serious."[116]

Not only did Bohr fully recognize the profound chasm in the conceptual scheme of his theory, but he was convinced that progress in quantum theory could not be obtained unless the antithesis between quantum-theoretic and classical conceptions was brought to the forefront of theoretical analysis. He therefore attempted to trace the roots of this antithesis as deeply as he could. It was in this search for fundamentals that he introduced the revolutionary conception of "stationary" states, "indicating thereby that they form some kind of waiting places between which occurs the emission of the energy corresponding to the various spectral lines."[117] For he clearly realized

[111] "British Association: Problems of Radiation (from our special correspondent)," *The Times* (London), No. 40,316, Sept. 13, 1913, p. 10.

[112] REF. 108.

[113] N. Campbell, "The structure of the atom," *Nature 92*, 586–587 (1913).

[114] N. Bohr, "Om Brintspektret," *Fysisk Tidsskrift 12*, 97–114 (1914); reprinted, *ibid. 60*, 185–202 (1963); English translation, "On the spectrum of hydrogen," in N. Bohr, *The Theory of Spectra and Atomic Constitution* (Cambridge University Press, 1922), pp. 1–19.

[115] *Ibid.*, p. 100; p. 4.

[116] *Ibid.*, p. 105; pp. 9–10.

[117] *Ibid.*, p. 107; p. 11.

that Planck's idea of a discontinuity in energy emission—the very idea which probably suggested to him the notion of "stationary states" as "waiting places" ("Holdepladser")—was foreign to classical physics, irreconcilable with it, but nevertheless legitimate and necessary. It was in this search for fundamentals that he generalized the derivation of Rydberg's constant from its first version, based on Planck's formula, to its last formulation, based on "a connection with the ordinary conceptions."[118] This analogy, however, he stressed time and again, should not be misleadingly interpreted as an analogy in the foundations. For "nothing has been said here about how and why the radiation is emitted."[119] Concluding his address, Bohr declared: "I hope I have expressed myself sufficiently clearly so that you appreciate the extent to which these considerations conflict with the admirably coherent group of conceptions which have been rightly termed the classical theory of electrodynamics. On the other hand, by emphasizing this conflict, I have tried to convey to you the impression that it may also be possible in the course of time to discover a certain coherence in the new ideas."[120]

We thus see that, contrary to Planck and Einstein, Bohr did not try to bridge the abyss between classical and quantum physics, but from the very beginning of his work, searched for a scheme of quantum conceptions which would form a system just as coherent, on the one side of the abyss, as that of the classical notions on the other side of the abyss.[121]

118 *Ibid.*, p. 108; p. 13.

119 *Ibid.*, p. 108; pp. 12–13.

120 *Ibid.*, p. 114; p. 19.

121 For a penetrating analysis of this aspect of Bohr's work, from the viewpoint of the Copenhagen interpretation, cf. K. M. Meyer-Abich, *Korrespondenz, Individualität und Komplementarität* (Dissertation, University of Hamburg, 1964), published as vol. 5 in the series "Boethius—Texte und Abhandlungen zur Geschichte der exakten Wissenschaften," edited by J. E. Hofmann, F. Klemm, and B. Sticker (Franz Steiner Verlag, Wiesbaden, 1965).